COMPARISON ON THE DURABILITY OF DIFFERENT PORTLAND CEMENTS AFTER FIVE YEARS EXPOSURE TO SULFATE AND TO SEA WATER ATTACK

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Abstract
Experimental research has been performed to relate specific cement characteristics to deterioration due to sulfate and sea water attack after five year exposure, and to study different test method suitability for sulfate and marine resistance. Sulfate resistance testing have been performed on mortar specimens made with fifteen cement types of statistically diverse chemical composition according to European standard EN 197-1, most of them with sulfate resistant properties according to Spanish regulations. Chemical and mechanical characteristics were studied to determine the variation in properties of selected cements. SO_3 content, type and amount of additions, C_3A, and C_4AF content were used to examine relationships between these characteristics and the results of sulfate resistance. Mortar specimens testing using Na_2SO_4 as the aggressive medium according to ASTM 1012 (with w/c ratio adapted to prENV 196-X:1995) was performed using each type of cement; identical specimens were also stored in sea water, and in lime saturated water (blank condition), up to five year age. Additionally these cements were tested conforming ASTM 452 and Koch and Steinegger test. Recommended acceptance limits for sulfate resistance of cements concerning to each used test method were evaluated in order to explore their suitability. Relationships between cement characteristics, degradation, expansive products obtained by X-ray diffraction techniques and maximum expansion after applied storage treatments, were correlated at final age, to redefine cement characteristics for sulfate resistant and marine resistant Portland cement.

Originality
In the last century many studies had been developed with traditional Portland cements to provide meaningful discrimination between sulfate resistant or non-sulfate resistant cements. In this investigation fifteen real trading common cements (EN 197-1) have been tested. Different C_3A contents, variable types and proportioning of constituents (limestone, pozzolanic additions, blastfurnace slag ...) with or without the same clinker type were investigated. Present theories about accelerated test procedures adopt that the mechanism of deterioration in the accelerated test should be representative of those observed in service. In this study linear expansion and external damage of mortar specimens with a w/c ratio of 0,5 have been tested, and both have been analysed after five years of immersion in a sulfate solution and also in seawater (and in lime saturated water, as a blank condition). None of the prepared mortars was blended with gypsum or any other non realistic condition. Additionally these european common cements were tested following ASTM standards (modified to EN 196-1 mortar compositions) to evaluate if ASTM specifications were applicable to both cement families of such different characteristics.

Chief contributions
The development of a prescriptive European Standard (EN) for sulfate resisting cements has been a difficult task due to differences in the types of cements that are considered sulfate resisting. Many countries have national specifications for sulfate resisting cements, most of them only specifying the cement chemical composition, but these regulations do not exactly coincide. This research provides newer information and proposes criteria taking into account the behaviour of common cements, useful to unify the different values established in various national european regulations, which probably were mainly based on traditional Portland cements. These results are in agreement with a broad spectrum of sulfate expansion theories and can provide a better way to specify sulfate resistant cements, establishing a relationship between some accelerated laboratory test and field performance after five year exposure. Durability behaviour in common cements conforming to EN 197-1 exposed to sulfate attack are explained, and also the correlation between sulfate resistance and seawater resistance has been studied.

Keywords: *sulfate attack, sea water attack, durability, expansion test*

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1. Introduction

Sulfate attack causes deterioration in concrete structures exposed to moist in sulfate-rich environments. The resistance to sulfate attack has long been considered to be connected to the characteristics of the cementitious material. However, the complex reactions in hydrating cement have made it difficult to isolate more than one variable at a time. In the last century many studies had been developed with traditional Portland cements to provide any meaningful discrimination between sulfate resistant or non-sulfate resistant cements. However in the 90's new work items were initiated directed towards the development of a performance test for sulfate resistance applicable for modern trading cements.

Experimental research has been carried out with fifteen EN 197-1 common cements according to the actual degree of technology production, all of them trading cements, involving not only different C_3A contents but using variable constituents types and proportioning (limestone, pozzolanic additions, blsatfurnace slag ...) with and without the same clinker type as well. Mortar specimens prepared from these types of cement have been cast to relate specific cement characteristics to expansion due to sulfate or sea water attack during five years, and to study different test method suitability for sulfate and marine resistance.

2. Experimental procedures

Materials

Fifteen trading cements with statistically diverse chemical composition were investigated to evaluate the effect of cement characteristics on sulfate resistance. All cements complied to EN 197-1, most of them with sulfate resistant properties according to Spanish regulations. Chemical and mechanical characteristics were studied to determine the variation in properties of selected cements. SO_3 content, type and amount of additions, C_3A and C_4AF content were used to develop relationships between these characteristics and the results of sulfate resistance. Chemical compositions and mechanical properties at 28 days of the cements are listed in Table 1.

Table 1: Chemical composition and mechanical properties

	Cement type and class	Chemical composition (weight, %)							Remarks	Compres. strength (MPa) (28 days)
		Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3		
1	CEM I 42,5 R (HSR)	1,73	20,7	3,81	3,92	63,4	1,1	2,87	HSR	54,7
2	CEM I 52,5 R	2,05	20,5	4,60	2,89	63,5	1,4	3,56	OPC	62,4
3	CEM II/B-V 42,5 R	1,57	27,9	5.76	2.96	55.5	1.2	3,05	20% fly ash	55,7
4	CEM I 42,5 R (HSR)	1,54	19,9	3,50	4,20	64,3	0,9	3,30	HSR	63,1
5	CEM IV/B(V) 32,5	3.48	39.6	3,00	2,76	46.2	0,8	2,80	24% fly ash	41,0
6	CEM II/B-L 32,5 N	11,27	16,0	3,04	2,94	62.1	0,8	3,00	26% limest.	42,9
7	CEM I 52,5 R	2,23	20,0	5,35	1,58	63,9	1,7	3,50	OPC	62,1
8	CEM I 42,5 R (HSR)	3,83	22,6	2,96	5,76	59,2	2,3	2,19	HSR	47,9
9	CEM II/A-L 42,5 R	7,47	20,0	2,27	0,26	65,7	0,5(*)	2,28	17% limest.	48,1
10	CEM II/A-V 42,5 R	2,91	24,5	4,54	2,94	58,1	2,9	3,06	6% fly ash	47,5
11	CEM I 52,5 N (HSR)	3,61	20,3	3,77	3,20	59,7	3,3	3,24	HSR	61,3
12	CEM III/A 42,5 N	4,22	22,9	6,15	2,38	55,0	1,2	3,27	36% slag	43,8
13	CEM I 42,5 R (HSR)	4,60	19,5	3,81	3,60	61,8	0,5	3,09	HSR	46,8
14	CEM I 42,5 R (HSR)	3.64	19,5	3,69	4,34	62,3	0,4	3,17	HSR	43,0
15	CEM I 52,5 N (HSR)	2.88	20,1	3,62	4,18	62,9	0,4	3,04	HSR	59,7

(*) White cement

Specimens and items of investigation

Cement samples were tested according to ASTM 452-02, with slight modificatios to approach this method to EN 196-1 European standard mortar composition. In ASTM C 452 procedure, cement is blended with finely divided gypsum to bring the SO_3 level to 7,0%, and the expansion of 25 mm x 25 mm x 285 mm mortar bars (1:2,75, w/c 0,485) placed in water at 23 ºC is determined at 14 days. For this experimental study mortar composition was modified according to EN 196-1 standard (1:3; cement:CEN calibrated sand, and w/c ratio 0,50). The expansion is expressed in percentage of total length (distance between the two bases of the measuring gauges studs embedded in both sides of each specimen).

In addition to mentioned expansion test, mortar specimens were tested using Na_2SO_4 as the aggressive medium according to ASTM 1012-04. In this standard, expansion of 25 mm x 25 mm x 285 mm mortar bars (1:2,75, w/c 0,485) is measured up to 12 months from the date they were initially submerged into the aggressive solution. Specimens were made as described previously for ASTM C 452 mortar mixes. For this experimental study mortar composition was modified according to EN 196-1 standard (1:3; cement:CEN calibrated sand, and w/c ratio 0,50) This test was performed using mortar specimens of each cement in a 50 g/l of Na_2SO_4 solution, but identical specimens were also stored in artificial sea water, and in lime saturated water (blank condition), up to five year age (3 specimens for each storage type). Expansion measurements were taken at 2 weeks, 1, 2, 3, 4, 5, 6, 9, 12, 15 ,18 and 21 months, 2, 3, 4 and 5 years.

Also 54 specimens of 40 x 40 x 160 mm for testing mechanical strength were made of each cement to be stored in a 50 g/l of Na_2SO_4 solution, in artificial sea water (composition per litre resulting of mixing: 30 g NaCl, 6 g $MgCl_2.6\ H_2O$, 5 g $MgSO_4.7\ H_2O$, 1,5 g $CaSO_4.2\ H_2O$ y 0,2 g $KHCO_3$), and in lime saturated water (blank condition), up to five year age (18 specimens for each storage type). The solutions were replenished once a year. The strength loss is computed at each of the test ages (6, 9, 12, 15, 18 and 60 months), and expressed as the ratio of the mean of the results obtained in the specimens covered by the aggressive solution divided by the mean of the values of the control specimens at same age in lime saturated water.

To study the different hydration and degradation products, specimens crushed at five year age were prepared and tested using qualitative X-ray diffraction (XRD).

Cement mortars were also tested conforming to Koch and Steinegger test. The procedure is based on making 28 prismatic mortar specimens (1 x 1 x 6 cm), proportioned to 1:1:2 (cement:fine sand:coarse sand by weight) with a water/cement ratio of 0,6. The aggressive agent is a 0,3 M sodium sulfate solution, obtained from 4,4% (by weight) anhydrous sodium sulfate. These 28 specimens are kept in distilled water at 20 ºC for 21 days, four of them are then tested for flexural strength and the other 24 are divided into two groups: 12 submerged in the aggressive solution and the other 12 in distilled water. At 15, 56 and 96 days, four specimens of each curing type were tested to determine flexural strength. The initial date is considered to be the end of the previous 21-day curing period. Strength loss is computed at each of the test ages, referred to control specimens, kept in distilled water.

3. Results and discussion

Periodic visual inspections of the 40 x 40 x 160 mm specimens were carried out, followed up with measurements of weight changes. After approximately two years, deterioration had started only on mortar samples 2 and 7 exposed in a 50 g/l of Na_2SO_4 solution. The outside appearance of both samples at four year age stored in sulfate solution showed a severe degradation (figures 1 and 2). No analogous external damages were observed on both mortar samples stored in artificial sea water (only fine microcracks on specimen surfaces).

Figure 1: Deterioration on sample 2 (specimen exposed at four years in sulfate solution)

Figure 2: Disintegration on sample 7 (specimen exposed at four years in sulfate solution)

To study different test methods suitability for sulfate and marine resistance, mineralogical composition and accelerated test results (Table 2) were correlated with mechanical tests carried out on samples exposed into aggressive solutions, to evaluate also if the specifications were applicable to both (ASTM on EN 197-1) cement families of such different characteristics.

Table 2: Mineralogical composition and mechanical/accelerated tests results

	Cement type and class	Mineralogical composition		Compressive strength loss in 34 g/l sulphate solution		Koch and Steinegger (strength loss)		ASTM C 452 14 days expansion (%)
		C_3A (%)	C_4AF (%)	18 months	60 months	56 days	96 days	
1	CEM I 42,5 R (HSR)	3,5	11,9	0,98	0,84	0,70	0,69	0,015
2	CEM I 52,5 R	7,3	8,8	0,81	0,20	0,64	0,60	0,037
3	CEM II/B-V 42,5 R	10,3	9,0	0,91	0,75	0,55	0,55	0,028
4	CEM I 42,5 R (HSR)	2,2	12,8	0,98	0,83	0,75	0,76	0,018
5	CEM IV/B(V) 32,5	3,3	8,4	0,90	0,91	0,89	0,85	0,024
6	CEM II/B-L 32,5 N	3,1	8,9	0,94	0,58	0,83	0,80	0,021
7	CEM I 52,5 R	11,5	4,8	0,79	0,00	0,46	0,05	0,042
8	CEM I 42,5 R (HSR)	0,0	16,0	1,04	0,92	0,74	0,73	0,011
9	CEM II/A-L 42,5 R	5,6	0,8	1,05	0,76	0,60	0,58	0,016
10	CEM II/A-V 42,5 R	7,1	8,9	1,00	0,87	0,95	0,97	0,026
11	CEM I 52,5 N (HSR)	4,6	9,7	1,02	0,72	0,94	0,92	0,019
12	CEM III/A 42,5 N	2,2	2,6	0,96	0,89	0,96	0,94	0,034
13	CEM I 42,5 R (HSR)	4,0	10,9	1,01	0,91	0,95	0,93	0,013
14	CEM I 42,5 R (HSR)	2,4	13,2	1,01	0,85	0,96	0,94	0,006
15	CEM I 52,5 N (HSR)	2,5	12,7	1,01	0,93	0,97	0,95	0,009

On Figure 3 strength loss after 18 and 60 months in 34 g/l sulfate solution storage is represented separately for CEM I cements and for cements with secondary constituents. OPC mortar specimens show an increase in compressive strength during the early stages of sulfate attack attributed to the reaction products formation, filling pores and air voids. At 60 months only CEM I cements with C_3A contents higher than 5% denote more than 50% strength loss. In specimens of Portland cement containing 26% of grinded limestone (sample 6, CEM II/B-L) a strength loss higher than 40% was reached. Comparing results at 18 and 60 months on Portland composite cements there was found no correlation between C_3A contents and strength loss.

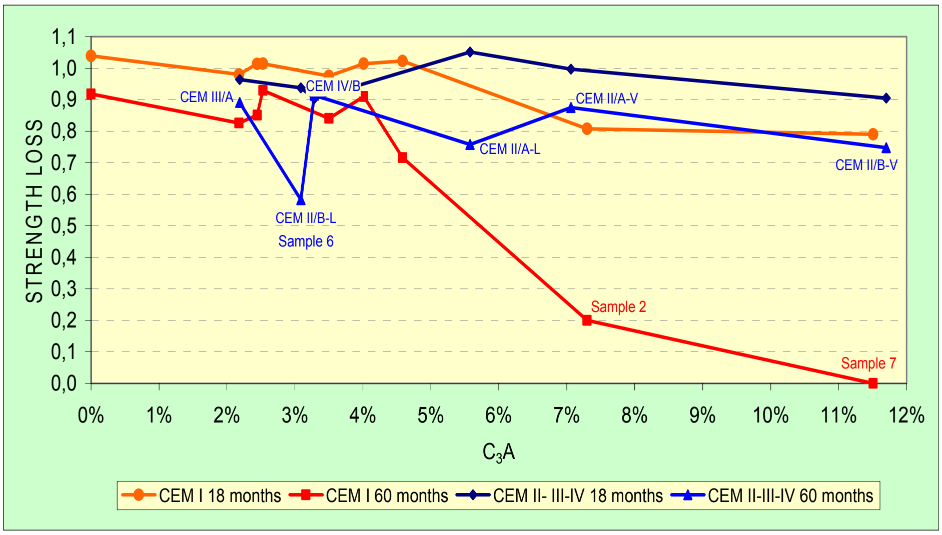

Figure 3: Strength loss after 18 and 60 months in 34 g/l sulfate solution storage

On CEM I cements with $C_3A \leq 4\%$ no correlation between C_3A contents and strength loss was revealed, either 18 months or 60 months results. European standard draft prEN 197-1 classifies CEM I cement as sulfate resistant if C_3A clinker content is found in one of these groups: 0%, ≤3% or ≤5%; for CEM IV demands $C_3A \leq 9\%$, and for CEM III/B or III/C no C_3A limitation is prescribed. According to obtained results this last group could be enlarged to involve CEM III/A cements. Probably it could be possible to join groups of 0% and 0-3% in CEM I-SR cements.

In Fig. 4a) and 4b) accelerated test results were compared with mechanical tests carried out after 60 months in sulfate solution storage. Strength loss trends (referred to C_3A content increase) in compressive test at 60 months and Koch-Steinegger flexural test do not match. Even resistance rate prescribed as Koch-Steinegger test requirement to define a cement as sulfate resistant (≥ 0,7) it would not be appropriate (classify several good performance CEM I cements as not useful). However downward trends of CEM I strength loss in compressive test and ASTM C 452 expansion test are quite similar.

ASTM C 150 permits a cement to be classified as a Type V sulfate resistant cement if expansion at 14 days following ASTM C 452 procedure is lesser than 0,040%. This is an optional requirement because cement can be classified as Type V if C_3A content is ≤ 5% and the sum of C_4AF + 2 C_3A ≤ 25%. Figure 4a) shows that these criteria are not suitable for the assessment of tested cements if mortar composition is according to EN 196-1 standard. For this cases an expansion requirement of 0,30% at 14 days can be proposed.

ASTM C 452 reports that this accelerated test method is not representative of the mechanism of deterioration observed in practice, and these criteria are not appropriate for the assessment of cement with secondary constituents such as blastfurnace slag and pozzolans, as represented in Fig. 4 b). Same conclusions could be applied to Koch-Steinegger test. Short timescale of both tests do not permit complete reaction of secondary constituents and the sulfate content has been introduced during mixing (only in ASTM C 452 test) so that effects of these additions in permeability reduction are not produced.

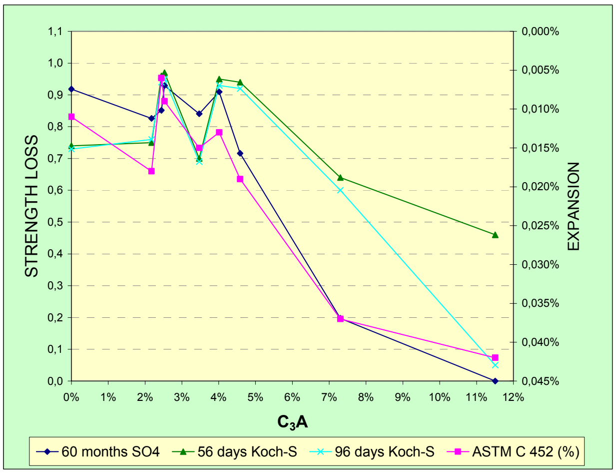

Fig. 4 a)

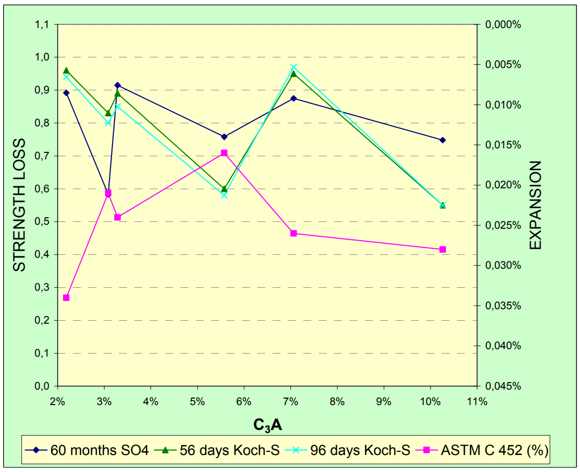

Fig. 4 b)

Figure 4: Strength loss at 60 months correlated with accelerated tests; a) OPC (CEM I); b) CEM II, III and IV

In Figure 5 linear expansion of mortar specimens are represented after storage in 34 g/l sulfate solution (Portland composite cements) or sea water storage (CEM I-C_3A content). Deterioration monitoring by linear expansion measurements is usually associated with the formation of ettringite from monosulfate. However at 60 months there was not found correlation between mechanical test results and gypsum, ettringite or Friedelt's salt detected in qualitative X-ray diffraction analysis. Strength results at 18 months of samples 2 and 7 indicate that deterioration has begun (20% strength loss) while showing relatively low levels of expansion, so conformity criteria for blended cements defined in ASTM 1012 (≤ 0,10% at 6, 12 or 18 months, depending on external aggressive conditions - ACI 201.2R) could not be suitable for the assessment of CEM I cements with EN 196-1 mortar composition. Expansion results of CEM I cements after 6, 12 or 24 months in sea water storage could be used as a guide of resistance behaviour, but not as a prescriptive requirement.

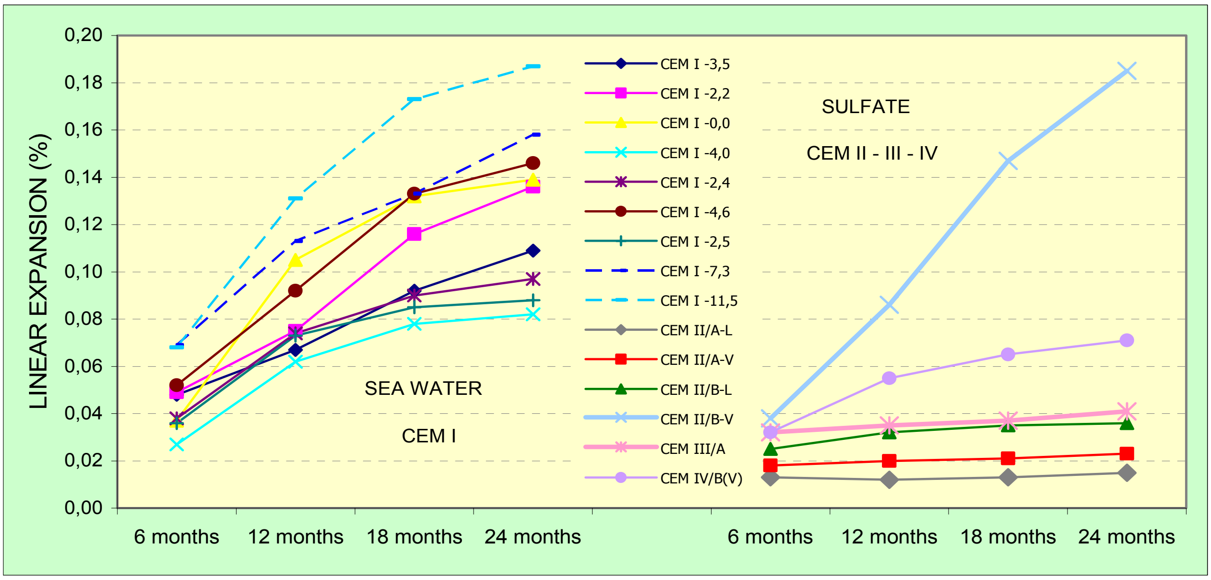

Figure 5: Linear expansion in 34 g/l sulfate solution or sea water storage

Expansion results according to ASTM 1012 of Portland composite cements (containing slag: CEM III/A; fly ash: CEM II/V and CEM IV; or limestone: CEM II/L) tested with EN 196-1 mortar composition are not useful as a prediction tool of strength loss behaviour. Only CEM II/A-V ($C_3A \approx 10\%$) could not comply with expansion requirements, confirming mechanical results and external damage at 60 months. However, Portland cement mortar containing 26% of limestone (CEM II/B-L) achieved a strength loss higher than 40% at 60 months, but expansion results were lower than the acceptance criteria.

4. Conclusions

After approximately five years of exposure in a sulfate solution 34 g/l, only in mortar specimens of CEM I (OPC) cements containing more than 5% of C_3A were observed disintegration or severe degradation, associated to subsequent formation of large amounts of massive gypsum and ettringite in the cracks. Also in mortar specimens of Portland composite cement containing a grinded limestone content of 26% were found compressive strength losses higher than 40%.

Different accelerated test methods were applied to evaluate sulfate resistance of cement samples: Koch-Steinegger test, ASTM C 1012 and ASTM C 452 (both ASTM methods adapted to mortar composition according to EN 196-1 standard). Koch- Steinegger acceptance criteria were not suitable for the assessment of most of analysed cements.

Instead of it, ASTM C 452 test adapted to EN 196-1 composition proved good performance when testing CEM I mortars: downward trends of CEM I strength loss in compressive test at 60 months and ASTM C 452 expansion results at 14 days were quite similar (profiles match almost exactly), so that it can be proposed an expansion requirement of 0,30% at 14 days for CEM I common cements.

ASTM C 1012 expansion test on specimens adapted to EN 196-1 mortar composition after 6, 12 or 24 months in sea water storage (CEM I) or 34 g/l sulfate solution (CEM II, CEM III or CEM IV) could be used as a guide of resistance behaviour, but not as a prescriptive requirement.

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